Transitions in Ferroelectric $KNbO_3$

G. Shirane, H. Danner, A. Pavlovic and R. Pepinsky

This report concerns developments supported at The Pennsylvania State College in part by Contract No. N6onr-26919 with the Acoustics Branch of the Office of Naval Research, and in part by Contract No. AF33(616)-2133 with the Aeronautical Research Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base.

R. Pepinsky
Project Director
X-Ray and Crystal Analysis Laboratory
Department of Physics
The Pennsylvania State College
State College, Pa.
15 October 1953

Submitted as a Letter to the Editor of the Physical Review.

Transitions in Ferroelectric $KNbO_3$*

G. Shirane, H. Danner, A. Pavlovic**

and R. Pepinsky,

X-Ray and Crystal Analysis Laboratory,

The Pennsylvania State College,

State College, Pa.

Dielectric measurements of $KNbO_3$ by Matthias and Remeika[1] revealed a ferroelectric Curie point at 435°C and a further transition at 225°C. An X-ray and optical study by Wood[2] revealed a cubic perovskite structure above the Curie point at 435°C, which transforms on cooling first to a tetragonal structure and then to an orthorhombic structure at the above two transition points. These transitions are related to the phase transitions in $BaTiO_3$ at 120°C and 0°C[3]. A further transition occurs in $BaTiO_3$ at -80°C, in which the structure changes from orthorhombic to rhombohedral. The above investigators found no significant change in the dielectric constant of $KNbO_3$ between room temperature and -190°C[1], and no optical change was observed between 25° and -50°C[2].

A preliminary dielectric study[4] carried out in our laboratory on $KNbO_3$ single crystals, prepared without flux, did show a sharp peak in the dielectric constant at -50°C on cooling and -35°C on heating, indicating the existence of a phase transition at this point. A further study has now been carried out on the dielectric, structural and thermal properties

of this lowest phase.

$KNbO_3$ single crystals were prepared as described by Wood[2], using KCO_3 as a flux and cooling down from 1000°C. The crystals were generally rectangular, transparent, light-yellow plates. Optical observation showed them to be multi-domain crystals. Dielectric tests were made on crystals 2-3 mm on edge and about 0.3 mm in thickness.

Figure 1 shows the dielectric constant vs. temperature curve measured at 10 kc/sec and a field strength of about 5v/cm. The heating and cooling rate was about 1°C/min. In agreement with previous data, this curve shows a very sharp change in dielectric constant at 220° and 420°C on heating. In addition to these, there is an abrupt change in the dielectric constant at -10°C on heating. On cooling, these three transitions occur at 410°, 200° and -55°C. A very large temperature hysteresis of about 45°C at the lowest phase change appears in the several crystals examined.

Powder photographs of $KNbO_3$ were taken with CuKα radiation in a Norelco powder camera of 11.4 cm diameter. Orthorhombic cell dimensions a = 5.721Å, b = 3.973Å, c = 5.695Å were obtained at room temperature, in good agreement with the previous data[2][5]. The lowest-temperature phase was examined in our low temperature camera, 10 cm diam., using CuKα radiation. Diffraction patterns at -140°C showed pseudo-cubic lines of perovskite type, but small although definite line splittings were observed in a few high angle lines such as (422), (332) and (420). The line splittings could be explained by assuming a rhombohedral lattice and considering both line spacings and intensities. Special attention was paid to the (400) reflections, which show no multiplet except that due to the α_1,α_2 doublet;

and this excluded the possibilities of tetragonal or orthorhombic lattices. The lattice parameters calculated from (422) and (332) line groups are $a = 4.016 \pm 0.002$ Å and $\alpha = 89^\circ\ 50' \pm 1'$.

Since $\alpha < 90^\circ$, this rhombohedral lattice is derived from an ideal cubic lattice by an elongation along [111]. This corresponds to the same lattice as that of the lowest phase in $BaTiO_3$. Polarizing microscope observations also showed the three phase transitions, at temperatures of the dielectric anomalies; and extinction positions are in accordance with the X-ray-determined symmetry of each phase. If we reduce the three transition temperatures by dividing by the Curie temperature, they are 1, 0.69, 0.49 and 1, 0.71, 0.38 for $BaTiO_3$ and $KNbO_3$ respectively. $KNbO_3$ is the only one perovskite-type ferroelectric which has been found to show three transitions similar to those of $BaTiO_3$.

To further compare the transitions in these two crystals, a study was made of the specific heat anomaly at the three transitions in $KNbO_3$. Ceramic $KNbO_3$ was prepared by firing a mixture of K_2CO_3 and Nb_2O_5 at 1050°C. An adiabatic calorimeter of the Nernst type[6], holding about 50 grams of $KNbO_3$ powder, was used for the lower temperature measurements. Another adiabatic calorimeter of Nagasaki-Takagi[7] type, containing about 15 grams of $KNbO_3$ powder, was used at high temperatures. The measurements were carried out by heating the specimens continuously at a rate of 0.5 to 1°C/min. Sharp peaks in the specific heats appeared at the three transition temperatures.

The values of the transition energies integrated from the curves are shown in Table I, together with data on $BaTiO_3$. The larger transition energies in $KNbO_3$ could be explained in terms of the larger lattice distortions in $KNbO_3$ as compared with the corresponding transitions in $BaTiO_3$. It may be interesting to point out that the relative ratio of the three entropy

changes are nearly the same in these two crystals; and, moreover, the entropy changes at the Curie points of these two crystals are approxi ately proportional to their $(\frac{c}{a}-1)$ values in the tetragonal phase.

To permit a more detailed comparison of these two crystals, and especially to apply the Devonshire's theory(8) of $BaTiO_3$ to $KNbO_3$, we must know the values of the Curie constant and the spontaneous polarization at the Curie point. Unfortunately, reliable values of these quantities in $KNbO_3$ are difficult to obtain, because of the relatively high conductivity near the Curie point at 430°C.

The authors express their gratitude to Mr. R. E. Newnham for preparation of the single crystals.

*Research supported by Contract No. N6onr-26919 with Office of Naval Research, and Contract No. AF33(039)-12645 with Air Research and Development Command.

**Owens-Illinois Research Fellow.

(1) B. T. Matthias and J. P. Remeika, Phys. Rev. 82, 727 (1951).

(2) E. A. Wood, Acta Cryst. 4, 353 (1951).

(3) See for instance, A. Von Hippel, Rev. of Modern Physics 22 221 (1950).

(4) R. Pepinsky, R. Thakur and C. McCarty, Phys. Rev. 86, 650 (1952).

(5) P. Vousden, Acta Cryst. 4, 373 (1951).

(6) See for example, J. C. Southard and F. C. Brickwedde, J. Am. Chem. Soc. 55, 4378 (1933).

(7) S. Nagasaki and Y. Takagi, J. App. Phys. Japan 17, 104 (1948).

(8) A. F. Devonshire, Phil. Mag. (7) 40, 1040 (1949).

Table I. Transition Energy ΔE (cal/mole) and Entropy Change ΔS (cal/mole degree) at the Three Transitions in $BaTiO_3$ and $KNbO_3$

		Cubic ----	Tetragonal ----	Orthorhombic ----	Rhombohedral
$BaTiO_3$	ΔE	47 ~ 50[a,b,c]	16 ~ 26[a,b,c,d]	8 ~ 14[b,c,d]	
	ΔS	0.12 ~ 0.13	0.06 ~ 0.09	0.04 ~ 0.07	
$KNbO_3$	ΔE	190 ± 15	85 ± 10	32 ± 5	
	ΔS	0.28	0.17	0.12	

a. H. Blattner, W. Kaenzig and W. Merz, Helv. Phys. Acta, 22, 35 (1949).

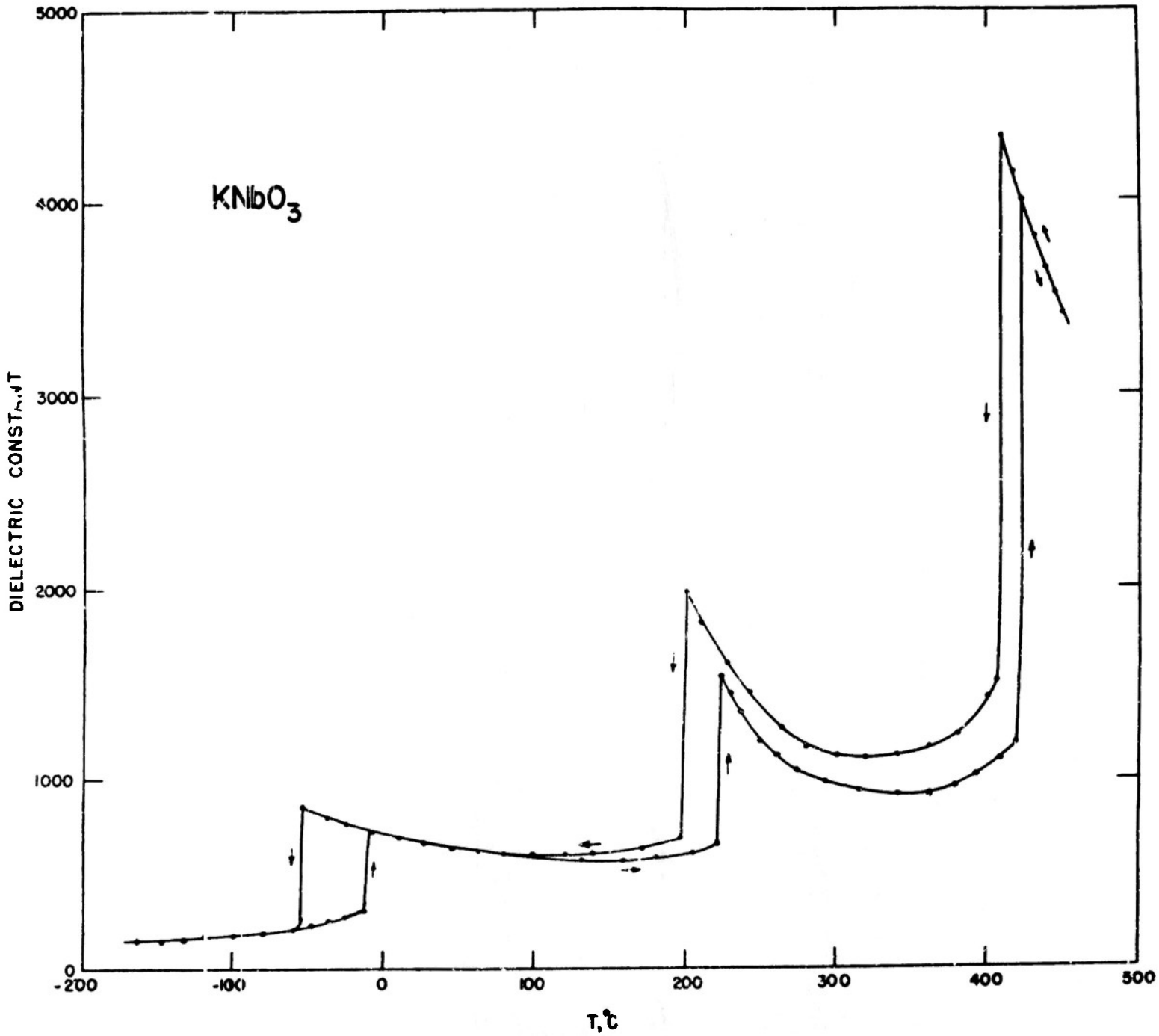
b. G. Shirane and A. Takeda, J. Phys. Soc. Japan 7, 1 (1952).

c. J. Volger, Philips Res. Rep. 7, 21 (1952).

d. S. S. Todd and R. E. Lorenson, J. Am. Chem. Soc. 74, 2043 (1952).

Figure 1

Dielectric Constant of $KNbO_3$


KNbO3
DIELECTRIC CONST.,εT
5000
4000
3000
2000
1000
0
-200
-100
0
100
200
300
400
500
T,°C